

Dynamics of stream nitrate sources and flow pathways during stormflows on urban, forest and agricultural watersheds in central Pennsylvania, USA

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Abstract:

Understanding the influence of storm events on nitrate (NO_3^-) dynamics is important for efficiently managing NO_3^- pollution. In this study, five sites representing a downstream progression of forested uplands underlain by resistant sandstone to karst lowlands with agricultural, urban and mixed land-use were established in Spring Creek, a 201 km² mixed land-use watershed in central Pennsylvania, USA. At each site, stream water was monitored during six storm events in 2005 to assess changes in stable isotopes of NO_3^- ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) and water ($\delta^{18}\text{O}-\text{H}_2\text{O}$) from baseflow to peakflow. Peakflow fractions of event NO_3^- and event water were then computed using two-component mixing models to elucidate NO_3^- flow pathway differences among the five sites. For the forested upland site, storm size appeared to affect NO_3^- sources and flow pathways. During small storms (<35 mm rainfall), greater event NO_3^- fractions than event water fractions indicated the prevalence of atmospheric NO_3^- source contributions at peakflow. During larger storms (>35 mm rainfall), event NO_3^- fractions were less than event water fractions at peakflow suggesting that NO_3^- was flushed from stored sources via shallow subsurface flow pathways. For the urbanized site, wash-off of atmospheric NO_3^- was an important NO_3^- source at peakflow, especially during short-duration storms where event water contributions indicated the prevalence of overland flow. In the karst lowlands, very low fractions of event water and even lower fractions of event NO_3^- at peakflow suggested the dominance of ground water flow pathways during storms. These ground water flow pathways likely flushed stored NO_3^- sources into the stream, while deep soils in the karst lowlands also may have promoted NO_3^- assimilation. The results of this study illustrated how NO_3^- isotopes and $\delta^{18}\text{O}-\text{H}_2\text{O}$ could be combined to show key differences in water and NO_3^- delivery between forested uplands, karst valleys and fully urbanized watersheds. Copyright © 2009 John Wiley & Sons, Ltd.

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INTRODUCTION

Excess nitrogen (N) in streams and rivers has resulted in large-scale eutrophication of coastal waters in the United States (Carpenter *et al.*, 1998; Howarth *et al.*, 2002; Boyer and Howarth, 2008), especially in estuarine systems such as the Chesapeake Bay (Boesch *et al.*, 2001). Although it is widely accepted that much of this N is exported as soluble nitrate (NO_3^-) during baseflow conditions (Schilling and Zhang, 2004), stormflow periods also are important because the addition of new water sources during storm events may mobilize new and distinctly different sources of NO_3^- than those at baseflow. Furthermore, other factors such as land-use (Jordan *et al.*, 1997) and geologic differences (Miller *et al.*, 1997) will exert unique influences on the mobilization and subsequent hydrologic transport of NO_3^- to streams during events. Understanding NO_3^- sources and flow pathways during baseflow and stormflow periods in watersheds with mixed land-use and geology is of principal interest to those managing NO_3^- pollution.

In terms of understanding NO_3^- sources, valuable insight has been gained by using NO_3^- isotopes ($\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$) (Kendall, 1998; Kendall *et al.*, 2007) to trace NO_3^- in mixed land-use watersheds (Chang *et al.*, 2002; Rock and Mayer, 2004; Segal-Rozenhaimer *et al.*, 2004; Panno *et al.*, 2006; 2008; Anisfeld *et al.*, 2007; Burns *et al.*, 2009). In general, sources of NO_3^- derived from sewage and animal manure are typically more enriched in $\delta^{15}\text{N}-\text{NO}_3^-$ (0 to +25‰) than NO_3^- originating from atmospheric deposition, fertilizers and microbial nitrification in soils (−10 to +7‰) (Kendall, 1998; Kendall *et al.*, 2007). Values of $\delta^{18}\text{O}-\text{NO}_3^-$ are typically very positive in atmospheric NO_3^- (greater than +30‰ using sealed glass tube method—Kendall *et al.*, 2007; greater than +60‰ using denitrifier method—Elliott *et al.*, 2007), which helps to distinguish NO_3^- in wet and dry deposition from NO_3^- formed via nitrification in soils (−10 to +15‰—Kendall, 1998; Kendall *et al.*, 2007).

Measuring changes in NO_3^- stable isotopes at baseflow and again at peakflow during storms on watersheds with different land-use would help paint a more complete picture of NO_3^- dynamics in streams. For example, studies by Ging *et al.* (1996) and Silva *et al.* (2002) showed

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that $\delta^{15}\text{N-NO}_3^-$ was a useful tracer of NO_3^- from sewage at baseflow, whereas increases in $\delta^{18}\text{O-NO}_3^-$ during storms were useful for inferring the importance of atmospheric NO_3^- in direct runoff from impervious surfaces during stormflow in two heavily urbanized watersheds in Austin, Texas. More recent studies by Anisfeld *et al.* (2007) and Burns *et al.* (2009) have also suggested that $\delta^{18}\text{O-NO}_3^-$ may indicate important shifts to atmospheric NO_3^- sources during high flows in urban and suburban watersheds. Similar studies in forested watersheds (Ohte *et al.*, 2004; Sebestyen *et al.*, 2008) have used $\delta^{18}\text{O-NO}_3^-$ to show the importance of atmospheric NO_3^- in stream water during high flows following snowmelt runoff periods. Although changes in NO_3^- stable isotopes during storm events offer an opportunity to track important shifts in NO_3^- sources, these shifts only yield ancillary information on NO_3^- flow pathways and delivery mechanisms.

In this study, we apply traditional hydrograph separation using $\delta^{18}\text{O-H}_2\text{O}$ (Sklash, 1990; Pionke *et al.*, 1993; DeWalle and Pionke, 1994) and extend this idea to NO_3^- stable isotopes to simultaneously calculate and compare event fractions of water and NO_3^- during storm events. We define event NO_3^- as the fraction of new NO_3^- added to the stream at peakflow during an individual storm event. By directly comparing estimated fractions of event water and event NO_3^- for the same storm events, we can ascertain potentially important differences in flow pathways for water and NO_3^- among watersheds with different land-use and geology. For example, we hypothesize that additions of wet NO_3^- deposition and wash-off of dry NO_3^- deposition during storms may result in fractions of event NO_3^- that are greater than fractions of event water. In contrast, assimilative processes and

flushing of stored NO_3^- sources that have undergone biogeochemical transformations may result in fractions of event NO_3^- that are less than fractions of event water. Our intent was to combine information on event NO_3^- and event water at peakflow with observed changes in NO_3^- stable isotopes from baseflow to peakflow to shed additional light on NO_3^- flow pathways and delivery mechanisms in mixed land-use watersheds during storms.

MATERIALS AND METHODS

Spring Creek watershed

The Spring Creek watershed is located in central Pennsylvania and is a tributary to the Susquehanna River, which eventually flows into the Chesapeake Bay estuary (Figure 1). Central Pennsylvania has a humid, temperate climate, with mean daily temperatures ranging from -1°C during the winter months to 19°C during the summer months. During 2005, the annual precipitation at State College, Pennsylvania, totalled 1043 mm, which was slightly more than the long-term mean annual precipitation of 970 mm (based on 80 years of data: 1926–2005) (Pennsylvania State Climatologist, 2007). Despite receiving slightly more than the average annual precipitation amount, streamflow at the United States Geological Survey (USGS) gauge in Houserville, Pennsylvania (Gauge# 01546400) (see Figure 1 for location), was approximately 39 cm in 2005, which was slightly less than the long-term mean annual flow of 42 cm based on 21 years of data (1985–2005).

Spring Creek is situated within the Appalachian Section of the Ridge and Valley Physiographic Province, which is characterized by sandstone and shale ridges (elevation ~ 550 – 600 m) and wide valleys with karst terrain

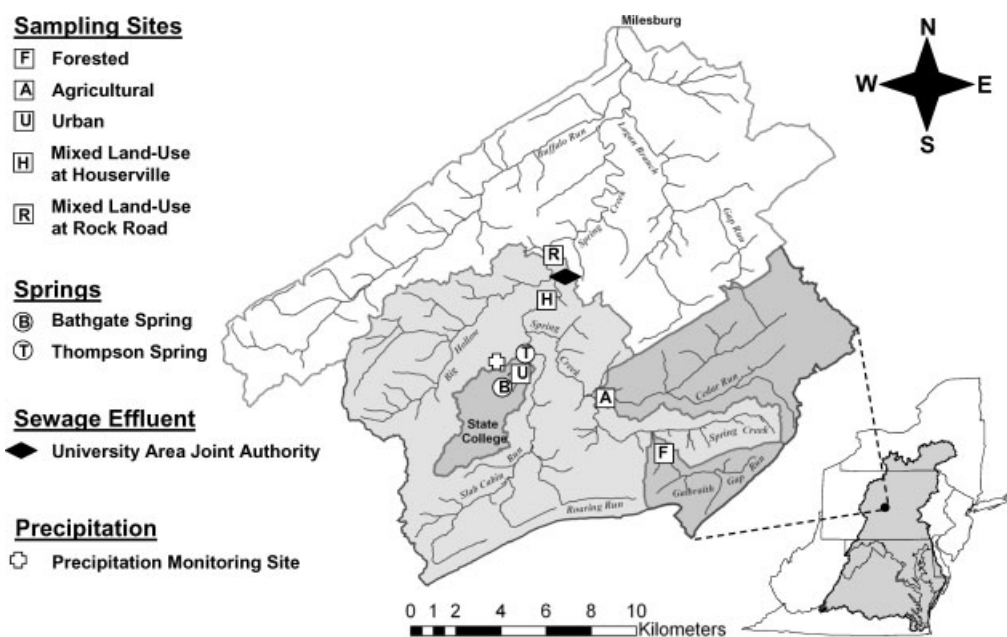


Figure 1. Map showing sampling sites and subwatershed boundaries within the upper Spring Creek watershed (light grey-shaded region in main panel). The lower right-hand panel shows the location of Spring Creek in central Pennsylvania and within the Chesapeake Bay watershed (grey-shaded region)

underlain by carbonate geology (elevation ~300–400 m). The complex geology found within the Spring Creek watershed is an important factor that affects the local hydrology. Upland forested watersheds have shallow soils with high infiltration capacities that are underlain by low permeability sandstone and shale bedrock. During storm events, runoff in these upland watersheds is typically generated via subsurface flow pathways that drain laterally downslope along the bedrock surface. This lateral subsurface flow can eventually produce saturation-excess overland flow at the base of hillslopes and in the near-stream zone (Fulton *et al.*, 2005). In contrast, streams that drain the karst valleys are fed by a combination of mountain runoff from the forested ridges and large ground water spring inputs (Fulton *et al.*, 2005; O'Driscoll and DeWalle, 2006). Due to the highly soluble limestone and dolomite bedrock, a significant portion of the carbonate valley aquifer is of the conduit flow type (Fulton *et al.*, 2005), which is characterized by large subsurface drainage pipes of considerable diameter (Shuster and White, 1971; White, 1988). These pipes can store and slowly release significant quantities of ground water during and several days after a storm event (White and Reich, 1970). During dry periods in the late summer and fall months, perched and losing streams are very common in the karst valley (O'Driscoll and DeWalle, 2006), especially in headwater regions.

Spring Creek is a mixed land-use watershed, with forests covering the ridges and a mixture of agriculture, residential and industrial land-use in the valleys. The watershed is undergoing rapid urbanization, with agricultural land-use being replaced by urban and suburban land-use. As a result of the continued development, a variety of significant point and nonpoint sources of NO_3^- pollution exist within the Spring Creek watershed, including one sewage treatment plant (University Area Joint Authority—UAJA) and runoff from agricultural and urban lands. Several miles of Spring Creek are listed

on the Federal 303(d) list for impairments due to nutrient pollution from point sources, urban runoff and crop-related agriculture (Pennsylvania Department of Environmental Protection, 2008). Sengle (2002) has shown that the main-stem of Spring Creek typically has NO_3^- concentrations ranging from 10 to 20 mg l^{-1} (2.3–4.5 mg l^{-1} as $\text{NO}_3\text{-N}$).

Watershed sampling design

The study was designed to take advantage of differences in land-use, geology and potential NO_3^- sources that existed within the upper portion of the Spring Creek watershed. Five watershed sampling sites were selected within the upper Spring Creek watershed (Figure 1), which included three tributary streams with uniquely different land-use (forest, agricultural and urban) as well as two downstream mixed land-use sites located on the main-stem of Spring Creek (Table I). This design allowed us to compare tracer values and NO_3^- sources among watersheds with different land-use and bedrock geology. Study sites were established on the following watersheds: (1) Galbraith Gap Run, a 13 km^2 forested watershed (95% of land area in forest); (2) Cedar Run, a 45 km^2 agricultural watershed (66% of land area in row crops and pasture); (3) Thompson Run, an 11 km^2 urban watershed (80% of land area with at least 30% impervious cover); (4) Spring Creek at Houserville, a 150 km^2 mixed land-use watershed; and (5) Spring Creek at Rock Road, a 201 km^2 mixed land-use watershed that is 3.7 km downstream of the site at Houserville (Figure 1) and is influenced by UAJA-treated municipal sewage effluent. The forested watershed is underlain by sandstone and shale bedrock (94%), whereas carbonate bedrock is the dominant geology in the agricultural (88%), urban (100%) and mixed land-use watersheds at Houserville (76%) and Rock Road (81%) (Berg *et al.*, 1980). The addition of the second mixed land-use site at Rock Road allowed us to assess the impacts of sewage discharges on NO_3^- concentrations and stable isotopes in Spring Creek. Treated

Table I. Information on sampling sites, predominant land-use classification, watershed area (km^2) and land-use^a distribution for each of the sites monitored in the upper Spring Creek watershed

Watershed	Site name	Area (km ²)	Forest			Agriculture		Impervious cover (%)			Other
			Decid.	Conif.	Mixed	Row crops	Pasture/ grass	5–30	31–74	>74	
<hr/>											
Galbraith Gap Run	Forested watershed	13	78	5	12	% of watershed area		1	0	0	0
Cedar Run	Agricultural watershed	45	26	0	1	42	24	3	2	1	0
Thompson Run	Urban watershed	11	7	0	1	2	5	3	51	29	1
Spring Creek at Houserville	Mixed land-use at Houserville	150	34	2	4	21	17	3	13	5	1
Spring Creek at Rock Road	Mixed land-use at Rock Road	201	32	1	3	19	16	3	17	6	2

Decid., Deciduous Forest; Conif., Coniferous Forest.

^a Based on information obtained from 2005 Pennsylvania land-use/land-cover dataset using the Anderson classification system (see: <http://www.pasda.psu.edu>).

Table II. Information on start and end times, antecedent precipitation (past month), observed precipitation type, precipitation amount and storm characterization for the six storms sampled during 2005

Storm number/date	Description	Duration (h)	Antecedent precipitation—past month (mm)	Precipitation characteristics			
				Type	Amount (mm)	Mean intensity (mm h^{-1})	Number of sequential samples obtained
1. 23 March 2005	Storm moving along stalled frontal boundary	10	110	Rain/Snow	12.2	1.0	3
2. 28–29 March 2005	Atlantic coastal storm—Nor'easter	32	127	Rain	61.0	2.0	8
3. 5 July 2005	Cold frontal passage—thunderstorm	2	44	Rain	35.4	18.0	2
4. 31 August 2005 ^a	Cold frontal passage—thunderstorm	1	46	Rain	49.0	49.0	2
5. 7 October 2005 ^b	Storm moving along stalled frontal boundary	13	23	Rain	87.0	6.7	5
6. 16 November 2005	Cold frontal passage	5	89	Rain	13.7	2.7	3

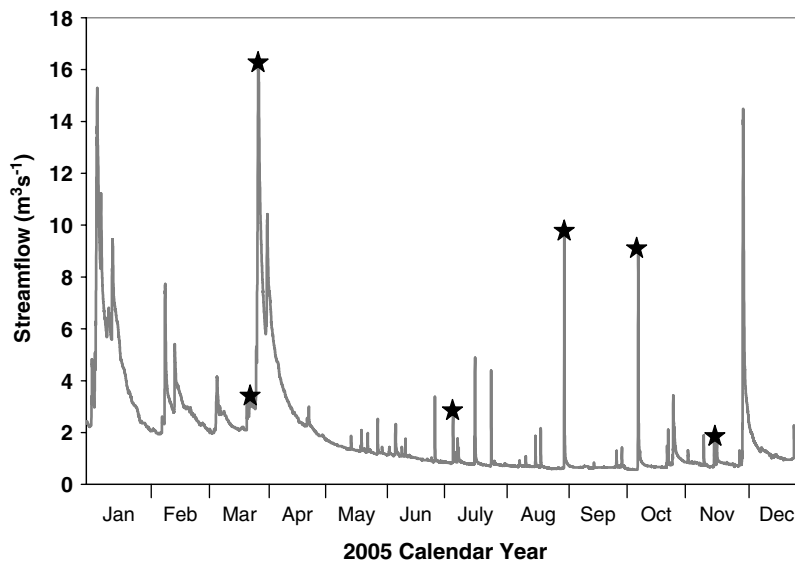
^a Remnants of Hurricane Katrina.^b Remnants of Tropical Storm Tammy.

Figure 2. Spring Creek at Houserville hydrograph for 2005 showing the six storm events that were sampled (black stars)

sewage effluent was collected at the UAJA outfall along Spring Creek located about 1.4 km downstream of the Houserville sampling site (Figure 1). Finally, two ground water springs in karst terrain (Figure 1) were sampled once in summer and once again in late fall to characterize the chemistry and stable isotopic composition of shallow ground water.

Stream sampling and precipitation monitoring during storms

All stream sites and the sewage treatment plant effluent were sampled during six storm events of different magnitude, intensity and duration in 2005. This allowed us to characterize a range in hydrological response among the five watersheds. Table II provides information on the individual storm events. For additional details on the origin and evolution of each storm, the reader is referred

to Buda (2007). Figure 2 summarizes the hydrologic response to each storm event based on 15-min streamflow rates measured at the USGS gauge on Spring Creek in Houserville, Pennsylvania (Gauge# 01546400).

For each storm event, streams were sampled once during antecedent baseflow and again at or near peakflow. Baseflow samples were typically collected within 24 h of the impending storm and were used to reflect local ground water inputs for each stream site. The sewage treatment plant effluent was only sampled once per storm during baseflow conditions.

Precipitation during each event was sampled using a sequential passive precipitation sampler designed and constructed to collect sufficient volumes of rainwater for NO_3^- stable isotope and inorganic chemical analysis. The sampler was constructed from a polyethylene plastic tarp, approximately 5.7 m^2 in area, which funnelled water

to a series of three 20-l polypropylene carboys. A new tarp was used for each event that was sampled, and the tarp was washed thrice with deionized water just before the onset of precipitation. Carboys were arranged such that they filled sequentially during storms according to a slightly modified design from that of Kennedy *et al.* (1979). Approximately 3.6 mm (0.14 inch) of rainfall filled an individual carboy. Once three sequential carboys were filled with rainwater (~10.8 mm of rainfall), three clean carboys were brought in to replace the full ones. This process was repeated during large precipitation events, which enabled within-storm variations of stable isotopes and chemistry to be evaluated. Subsamples or rainwater were collected from individual carboys for inorganic chemistry and $\delta^{18}\text{O}$ - H_2O analysis. Finally, wash-off from the tarp was collected in a carboy after a 3-week long dry period in November 2005 to provide some information on the isotopic composition of dry NO_3^- deposition.

Water chemistry and stable isotope analysis

All stream water and precipitation samples were stored at 4 °C until they could be analysed for inorganic chemistry at the Water Quality Laboratory in the Penn State Institutes of Energy and the Environment (PSIEE). Samples were analysed for pH, specific conductance, nitrate-N (NO_3^- -N) and ammonium-N (NH_4^- -N). All analyses were conducted using standard methods (American Public Health Association, 2005).

Stable isotopes in NO_3^- ($\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^-) were analysed according to the methods outlined by Chang *et al.* (1999) and Silva *et al.* (2000). Briefly, anion exchange resins were used to collect dissolved NO_3^- in all water samples. Silva *et al.* (2000) showed that anion exchange resins loaded with NO_3^- can typically be stored for up to 1 year at 4 °C with minimal effects on $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- . In this study, anion exchange resins loaded with NO_3^- were stored at 4 °C until they could be shipped to the University of Waterloo Environmental Isotope Laboratory (EIL) for further processing and analysis, usually within 1–2 months of collection. More specific details on the analytical methods used by the University of Waterloo EIL are given in Spoelstra *et al.* (2004). The results for $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- are reported in delta notation ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in permil units, ‰) versus their respective international reference standards: N_2 gas for $\delta^{15}\text{N}$ - NO_3^- and Standard Mean Ocean Water (SMOW) for $\delta^{18}\text{O}$ - NO_3^- . The analytical error for both isotopes was approximately $\pm 0.2\text{‰}$ based on duplicate samples (26 duplicates for $\delta^{15}\text{N}$ - NO_3^- and 14 duplicates for $\delta^{18}\text{O}$ - NO_3^-).

Oxygen-18 in water ($\delta^{18}\text{O}$ - H_2O) was also analysed at the University of Waterloo EIL. Water samples for $\delta^{18}\text{O}$ - H_2O were collected and stored in airtight 20-ml HDPE scintillation bottles before shipment to the EIL at Waterloo. The analysis for $\delta^{18}\text{O}$ - H_2O was conducted using the CO_2 equilibration method outlined by Epstein and Mayeda (1953). All results are reported in delta notation

($\delta^{18}\text{O}$ in permil units, ‰) relative to SMOW. The analytical error for $\delta^{18}\text{O}$ - H_2O isotopes was approximately $\pm 0.1\text{‰}$ based on 20 duplicate samples.

Data analysis

The two-component mixing model (Equation 1) has been commonly used by hydrologists to separate peak-flow into its 'pre-event' (old) and 'event' (new) components using conservative tracers such as $\delta^{18}\text{O}$ - H_2O isotopes (Pionke *et al.*, 1993; DeWalle and Pionke, 1994). The two-component model is summarized below:

$$\text{Event Fraction} = (\delta_T - \delta_P) / (\delta_E - \delta_P) \quad (1)$$

where δ_T = peakflow isotope or chemical concentration (measured at peak streamflow during the event); δ_P = pre-event isotope or chemical concentration (measured at baseflow immediately before the event); δ_E = event isotope or chemical concentration (measured in precipitation).

The two-component model was used to separate pre-event and event water fractions on all five watersheds using $\delta^{18}\text{O}$ - H_2O . $\delta^{18}\text{O}$ - H_2O was selected because it is considered a more direct tracer for sources of water than other conservative tracers such as dissolved SiO_2 (Wels *et al.*, 1991).

The new approach applied in this study was to use NO_3^- stable isotopes to partition peakflow NO_3^- into its 'pre-event' and 'event' source fractions using Equation (1). $\delta^{18}\text{O}$ - NO_3^- was selected as the tracer to perform these calculations because it exhibited better separations between precipitation (event NO_3^-) and terrestrial NO_3^- (pre-event NO_3^-) sources. Comparisons of event water to event NO_3^- were used to help interpret potential sources and flow pathways of NO_3^- during storm events.

According to Sklash (1990) and Buttle (1994), users of two-component models in hydrology must assume that (1) δ_E does not vary while being routed through the watershed, (2) δ_P remains constant during the storm event, and (3) δ_P is significantly different from δ_E . With regard to the first assumption, precipitation represented event water, and therefore δ_E was measured in precipitation (Table III). During the course of all six storm events, significant variations of $\delta^{18}\text{O}$ - H_2O and NO_3^- stable isotopes in precipitation were observed (Table III) (Buda and DeWalle, in press). In order to assign an individual isotopic composition for event water and/or event NO_3^- (δ_E), a precipitation-weighted mean was calculated for each storm using the incremental mean method proposed by McDonnell (1990). With regard to the second assumption, recent research has shown that $\delta^{18}\text{O}$ - H_2O isotopes in pre-event water (δ_P) can vary significantly during storm events (Gremillion *et al.*, 2000a). In addition to $\delta^{18}\text{O}$ - H_2O variations, NO_3^- stable isotopes also may vary in baseflow during storm events. Although variations of $\delta^{15}\text{N}$ - NO_3^- and $\delta^{18}\text{O}$ - NO_3^- were minimal in

Table III. Summary statistics for relevant physical, chemical and stable isotope data for the five watersheds sampled at baseflow (BF) and peakflow (PF) in upper Spring Creek as well as sewage effluent from UAJA, ground water springs and precipitation

	Watershed												Sewage effluent	Springs	Precipitation
	Forested			Urban			Agricultural			Mixed LU					
	BF	PF		BF	PF		BF	PF		BF	PF				
Flow (mm d ⁻¹)	Mean	0.40	2.53	1.81	52.39	0.69	1.40	0.76	3.88	0.66	3.35	—	—	—	
	Min	0.07	0.27	0.71	9.35	0.33	0.50	0.33	0.93	0.34	0.90	—	—	—	
	Max	1.00	8.31	4.48	124.10	1.42	4.26	1.73	9.30	1.38	7.63	—	—	—	
Temp. (°C)	Mean	11.1	11.8	14.6	15.5	12.5	13.4	12.2	13.3	14.1	13.9	18.0	12.0	—	
	Min	4.5	4.2	10.8	6.2	7.8	6.4	7.1	4.9	7.1	5.6	11.4	10.6	—	
	Max	17.6	18.4	16.9	23.4	17.5	19.3	18.0	20.8	20.2	20.2	23.0	15.5	—	
EC ^a (μS cm ⁻¹)	Mean	37	52	637	140	488	450	532	363	642	420	911	695	12	
	Min	29	32	594	74	453	399	438	215	497	266	776	615	2	
	Max	43	86	694	321	518	533	613	527	771	607	1077	770	35	
pH	Mean	7.5	7.6	8.2	8.2	8.2	8.0	8.3	7.9	8.1	7.9	7.3	7.5	5.0	
	Min	6.9	7.0	8.0	7.9	8.0	7.8	8.2	7.7	8.0	7.8	6.9	7.4	4.2	
	Max	8.6	8.4	8.3	8.5	8.3	8.2	8.3	8.1	8.3	8.0	8.0	7.7	6.7	
NO ₃ ⁻ (mg l ⁻¹)	Mean	0.7	1.6	19.3	2.9	20.9	17.3	15.4	9.3	24.1	12.6	40.9	19.8	0.8	
	Min	0.3	1.1	16.6	1.0	17.1	14.1	11.6	5.3	16.2	6.5	28.8	18.1	0.2	
	Max	0.9	2.3	23.0	5.9	28.8	19.9	19.5	14.4	32.1	21.5	50.4	21.2	3.3	
δ ¹⁸ O-H ₂ O (‰)	Mean	-9.1	-8.7	-8.9	-8.5	-9.0	-8.8	-9.0	-8.4	-9.1	-8.58	-9.1	-9.0	-8.3	
	Min	-9.3	-10.3	-9.5	-11.3	-9.3	-9.3	-9.6	-10.1	-9.4	-10.1	-9.4	-9.1	-16.7	
	Max	-8.9	-7.2	-8.5	-4.8	-8.9	-8.2	-8.7	-6.7	-8.7	-6.9	-8.9	-8.7	-3.6	
δ ¹⁵ N-NO ₃ ⁻ (‰)	Mean	1.4	1.3	6.9	2.8	5.1	5.2	5.8	5.4	10.9	7.8	14.8	5.5	0.2	
	Min	0.0	0.3	5.2	-2.5	4.2	4.6	5.0	5.0	8.4	6.9	9.9	4.6	-5.6	
	Max	2.6	2.9	10.4	6.2	7.2	6.0	8.3	5.9	12.7	9.6	18.1	6.6	5.0	
¹⁸ O-NO ₃ ⁻ (‰)	Mean	4.9	15.9	3.7	30.8	3.7	2.9	3.5	5.4	4.7	5.4	2.2	2.4	44.3	
	Min	0.4	11.3	1.7	11.4	2.3	1.9	1.6	4.5	2.8	2.5	-0.2	1.8	11.9	
	Max	13.6	22.4	5.8	49.9	7.3	4.0	6.6	7.2	8.2	10.4	4.6	2.9	70.0	

^a EC, electrical conductivity.

Spring Creek during non-storm periods (Buda, 2007), the variations of these isotopes in baseflow (δ_P) during storm events mostly were unknown. A study by Gremillion *et al.* (2000b) suggested that isotope variations in baseflow during storms did not adversely affect the results of steady-state two-component hydrograph separations in a Florida river. Therefore, we chose to use the simplified steady-state form of the two-component separation model (Equation 1) to calculate fractions of event water and event NO_3^- in the Spring Creek watershed.

RESULTS AND DISCUSSION

Baseflow conditions

General trends in NO_3^- concentrations. Concentrations of NO_3^- in stream water during baseflow conditions varied throughout the Spring Creek watershed, with generally high levels in the mixed land-use, urban and agricultural watersheds ($>15 \text{ mg l}^{-1}$) and much lower levels in the forested watershed ($<1 \text{ mg l}^{-1}$) (Table III). The highest baseflow NO_3^- concentrations were measured at the mixed land-use site at Rock Road (mean = 24.1 mg l^{-1} , SD = 5.8), which was the most downstream monitoring station used in the study (Figure 1). The high NO_3^- concentrations at Rock Road were influenced in part by a sewage treatment plant that was located approximately 2.3 km upstream, which discharged wastewater with very high NO_3^- (mean = 40.9 mg l^{-1} , SD = 8.2). Relatively high baseflow NO_3^- concentrations were also common in the agricultural (mean = 20.9 mg l^{-1} , SD = 4.2) and urban (mean = 19.3 mg l^{-1} , SD = 2.2) watersheds (Table III). Slightly lower baseflow NO_3^- concentrations were observed at the mixed land-use site in

Houserville (mean = 15.4 mg l^{-1} , SD = 2.8). In general, baseflow NO_3^- concentrations in all the karst watersheds were similar to those measured in two local ground water springs (mean = 19.8 mg l^{-1} , SD = 1.4). Baseflow NO_3^- concentrations at the forested watershed (mean = 0.7 mg l^{-1} , SD = 0.3) were by far the lowest of any of the five watersheds monitored during the study (Table III).

General trends in NO_3^- isotope values and sources. NO_3^- stable isotope data for all five watersheds at baseflow are given in Figure 3. Although values of $\delta^{18}\text{O}-\text{NO}_3^-$ showed very little spread across the five watersheds (Figure 3), values of $\delta^{15}\text{N}-\text{NO}_3^-$ varied more substantially owing in part to the influence of different land-use and potential NO_3^- sources affecting each stream. The forested watershed had the lowest $\delta^{15}\text{N}-\text{NO}_3^-$ (mean = $+1.4\text{‰}$, SD = 1.0) of all five watersheds. In general, NO_3^- isotope values on the forested watershed plotted within the range of NH_4^+ in rainfall and soil N (Figure 3). Values of $\delta^{15}\text{N}-\text{NO}_3^-$ in stream water on the agricultural watershed (mean = $+5.1\text{‰}$, SD = 1.1) and mixed land-use site at Houserville (mean = $+5.8\text{‰}$, SD = 1.2) were generally similar at baseflow (Figure 3; Table III). Although the majority of NO_3^- isotope data obtained from the agricultural watershed and the mixed land-use site at Houserville fell in the range of soil N (Figure 3), a few higher values of $\delta^{15}\text{N}-\text{NO}_3^-$ (greater than $+7\text{‰}$) suggested a potential influence of animal waste. The highest $\delta^{15}\text{N}-\text{NO}_3^-$ measurements in baseflow were recorded at the mixed land-use site at Rock Road (mean $+10.9\text{‰}$, SD = 1.8) indicating a clear influence of NO_3^- from sewage effluent

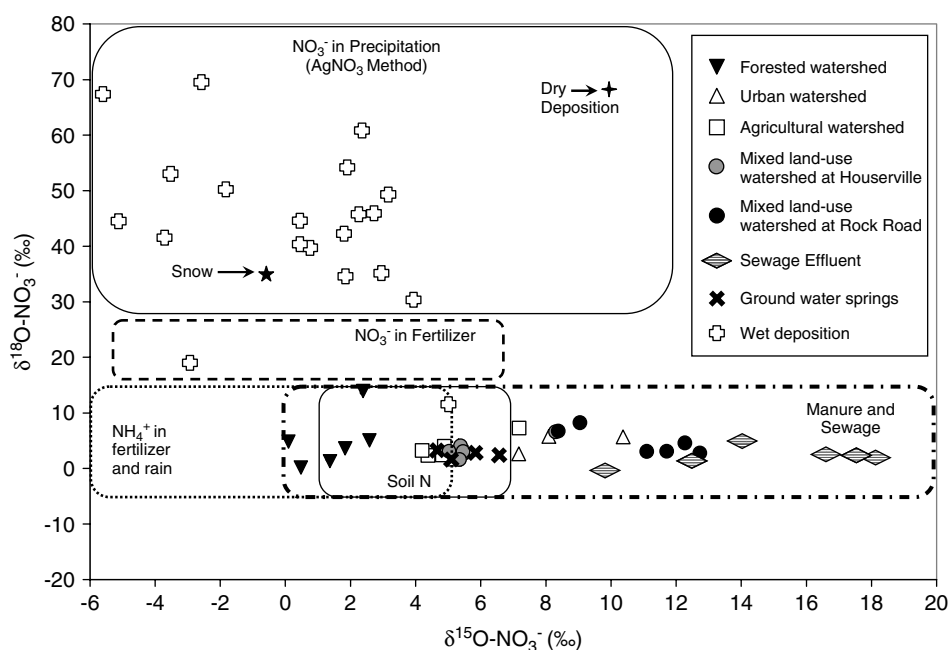


Figure 3. $\delta^{18}\text{O}-\text{NO}_3^-$ versus $\delta^{15}\text{N}-\text{NO}_3^-$ plot showing baseflow samples of stream water collected from the five watersheds in Spring Creek. Nitrate isotope data are also plotted for samples of sewage effluent, ground water springs and NO_3^- in wet deposition. A melted snow sample collected on 23 March 2005 and a dry deposition sample collected on 15 November 2005 are also shown. Boxes outlined on the plot indicate approximate boundaries for the isotopic composition of different sources of NO_3^- according to Kendall *et al.* (2007)

(Figure 3), which discharged into Spring Creek approximately 2.3 km upstream and had a mean $\delta^{15}\text{N-NO}_3^-$ value of $+14.8\text{‰}$ (SD = 3.2) (Table III; Figure 3). The urban watershed showed considerably more variation in $\delta^{15}\text{N-NO}_3^-$ (mean = $+6.9\text{‰}$, SD = 2.1) at baseflow than the other four watersheds (Figure 3), suggesting that urban stream water was a mixture of soil N and NO_3^- from animal waste or sewage.

Storm events

NO_3^- isotopes in wet and dry deposition. In wet deposition, $\delta^{15}\text{N-NO}_3^-$ (mean = $+0.2\text{‰}$, SD = 3.7) and $\delta^{18}\text{O-NO}_3^-$ (mean = $+44.3\text{‰}$, SD = 14.6) data generally plotted within the range of previous studies (Figure 3) (Kendall *et al.*, 2007 and references therein), and showed considerable variability within (Buda and DeWalle, in press) and between storm events (Figure 3, Table III). Values of $\delta^{18}\text{O-NO}_3^-$ in wet deposition that were less than $+30\text{‰}$ (Figure 3) may have been due to the use of the AgNO_3 method (Chang *et al.*, 1999; Silva *et al.*, 2000), which has been shown to produce lower $\delta^{18}\text{O-NO}_3^-$ values than the more recently developed denitrifier method (see Kendall *et al.*, 2007 for a more thorough discussion of this issue). In addition to wet deposition samples, one melted snow sample was collected on 23 March 2005 ($\delta^{15}\text{N-NO}_3^- = -0.6\text{‰}$; $\delta^{18}\text{O-NO}_3^- = +34.7\text{‰}$) during a rain-on-snow event (Table II). Of further note is a dry deposition sample collected before a storm in November 2005 ($\delta^{15}\text{N-NO}_3^- = +9.9\text{‰}$; $\delta^{18}\text{O-NO}_3^- = +68.5\text{‰}$) that was much more enriched in $\delta^{15}\text{N-NO}_3^-$ than samples of wet deposition. This trend of higher $\delta^{15}\text{N-NO}_3^-$ in dry deposition as compared with wet deposition is generally consistent with what has been observed in some previous studies (Elliott *et al.*, in press; Kendall *et al.*, 2007 and references therein).

Forested watershed response to storm events. NO_3^- sources: The forested watershed (Figure 1) exhibited

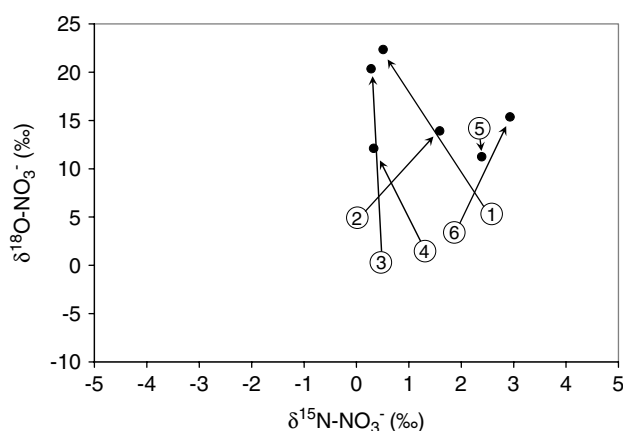


Figure 4. Forested watershed $\delta^{18}\text{O-NO}_3^-$ versus $\delta^{15}\text{N-NO}_3^-$ for all six storm events sampled during 2005 showing baseflow (open numbered circle) to peakflow (closed black circle) changes in NO_3^- stable isotopes. Numbers are used to label each storm event (1 = 23rd March; 2 = 28th–29th March; 3 = 5th July; 4 = 31st August; 5 = 7th October; 6 = 16th November)

interesting changes in NO_3^- stable isotopes during the six monitored storm events in 2005 (Figure 4). Although changes in $\delta^{15}\text{N-NO}_3^-$ from baseflow to peakflow were mostly small ($\pm 2.1\text{‰}$), changes in $\delta^{18}\text{O-NO}_3^-$ were consistently upward (mean increase of $+13.7\text{‰}$ for five storms), with the only exception being a slight decrease (-2.3‰) for the storm that occurred on 7th October (Figure 4). In addition, results from a two-tailed *t*-test indicated that $\delta^{18}\text{O-NO}_3^-$ during peakflow (mean = $+15.9\text{‰}$, SD = 4.5) was significantly higher than $\delta^{18}\text{O-NO}_3^-$ in baseflow (mean = $+4.9\text{‰}$, SD = 4.7) for all six storms ($p = 0.002$). This indicated that NO_3^- from the atmosphere, which typically had enriched values of $\delta^{18}\text{O-NO}_3^-$ (Table III), was important during peakflow conditions on the forested watershed.

Changes in $\delta^{15}\text{N-NO}_3^-$ and $\delta^{18}\text{O-NO}_3^-$ from baseflow to peakflow during storm events indicated that a mixture of atmospheric NO_3^- and N from soils were the two most important NO_3^- sources added during storm events (Figure 4). If we assume a $\delta^{18}\text{O-NO}_3^-$ value of $+5\text{‰}$ for microbially produced NO_3^- in forest soils (mean $\delta^{18}\text{O-NO}_3^-$ from six baseflow samples collected from the forested watershed), then the percent contribution of atmospheric NO_3^- to the forested watershed for all six storm events in 2005 could be estimated using the following two-component mixing equation (Williard *et al.*, 2001):

$$\% \text{ atmospheric } \text{NO}_3^- = [(\delta^{18}\text{O-NO}_3^- \text{ peakflow} - \delta^{18}\text{O-NO}_3^- \text{ soil}) / (\delta^{18}\text{O-NO}_3^- \text{ atmosphere} - \delta^{18}\text{O-NO}_3^- \text{ soil})] \quad (2)$$

The results of these calculations suggested that atmospheric NO_3^- accounted for approximately 33% of the NO_3^- in stream water during peakflow conditions in the forested watershed. These results mostly agreed with recent evidence using $\delta^{18}\text{O-NO}_3^-$ in other forested watershed studies, which generally have shown that atmospheric (wet + dry deposition) NO_3^- accounts for less

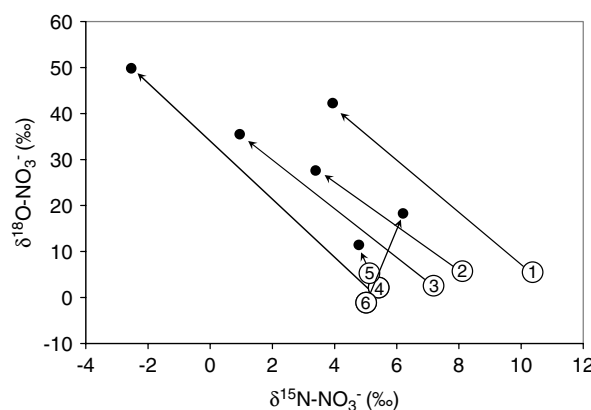


Figure 5. Urban watershed $\delta^{18}\text{O-NO}_3^-$ versus $\delta^{15}\text{N-NO}_3^-$ for all six storm events sampled during 2005 showing baseflow (open numbered circle) to peakflow (closed black circle) changes in NO_3^- stable isotopes. Numbers are used to label each storm event (1 = 23rd March; 2 = 28th–29th March; 3 = 5th July; 4 = 31st August; 5 = 7th October; 6 = 16th November)

than 30% of the total NO_3^- in stream water during storm events (Williard *et al.*, 2001) and snowmelt runoff episodes (Burns and Kendall, 2002; Campbell *et al.*, 2002; Piatek *et al.*, 2005; Sebestyen *et al.*, 2008). More recent work using $\delta^{17}\text{O}-\text{NO}_3^-$ in a semi-arid watershed showed that atmospheric NO_3^- may account for up to 40% of total NO_3^- exported during storms (Michalski *et al.*, 2004).

Results from the simple two-component models and the plots of NO_3^- stable isotopes in baseflow and peakflow (Figure 4) suggest that the majority of NO_3^- exported during storm events in the forested watershed was from microbial soil nitrification (67% of the NO_3^-). The observed NO_3^- isotope values in the peakflow mixture generally support this conclusion (Figure 4). Under ideal conditions (e.g., when soil moisture is low and soils are well aerated), microbial nitrification can produce significant pools of NO_3^- in the mineral soils, which then can be flushed into the stream during storm events (Creed *et al.*, 1996; Christopher *et al.*, 2008) due to the expansion of variable source areas (Creed and Band, 1998). This flushing mechanism appeared to be important on the forested watershed because NO_3^- concentrations consistently increased from baseflow to peakflow for all six storm events in 2005 (Table III) (mean increase = +0.9 mg l⁻¹).

NO_3^- flow pathways: Fractions of event NO_3^- and event water at peakflow in the forested, sandstone bedrock watershed appeared to vary for different types of storm events. Hydrograph separations using $\delta^{18}\text{O}-\text{H}_2\text{O}$ showed a large variation in responses on the forested watershed, with event water fractions ranging from 0.01 (23rd March) to 0.62 (29th March). When event NO_3^- fractions were compared with event water fractions on an event-by-event basis (Table IV), an interesting pattern emerged that appeared to indicate an effect of storm size on flow path responses. In general, small storms (<35 mm rainfall) produced fractions of event NO_3^- that were greater than fractions of event water. In contrast,

larger storms (>35 mm rainfall) produced fractions of event NO_3^- that were less than fractions of event water.

During the three largest storm events (29th March, 31st August and 7th October), it appeared that potential increases in $\delta^{18}\text{O}-\text{NO}_3^-$ in stream water from atmospheric NO_3^- inputs with high $\delta^{18}\text{O}-\text{NO}_3^-$ values (greater than +30‰) may have been reduced by significant fluxes of NO_3^- from soil water sources that typically have much lower $\delta^{18}\text{O}-\text{NO}_3^-$ values (less than +13‰) (Mayer *et al.*, 2001; Spoelstra *et al.*, 2007). Soils in the forested sandstone uplands are relatively shallow, compared with soils in the karst valleys, and rapid mobilization of soil NO_3^- in large events is quite possible. Additionally, evidence using $\delta^{18}\text{O}-\text{H}_2\text{O}$ in Appalachian forested watersheds points to the rapid mobilization of soil water through macropores and other preferential flow pathways as an important source of streamflow during large storm events (Swistock *et al.*, 1989). If this type of flow path was active during the three largest storm events, then high event water contributions and flushing of soil-derived NO_3^- with low $\delta^{18}\text{O}-\text{NO}_3^-$ could represent a plausible explanation for fractions of event NO_3^- that were less than fractions of event water.

During the three smallest storm events (23rd March, 5th July and 16th November), event NO_3^- sources appeared to be more important than pre-event NO_3^- sources from soils as evidenced by fractions of event NO_3^- that were greater than fractions of event water. Two non-competing hypotheses to explain this pattern include the influence of channel precipitation and wash-off of dry-deposited NO_3^- in throughfall, both of which have enriched $\delta^{18}\text{O}-\text{NO}_3^-$ relative to terrestrial NO_3^- sources. A study conducted in a forested Appalachian watershed in central Pennsylvania showed that the percentage of channel precipitation in stormflow was highest during small events, with overall contributions approaching 7% (Crayosky *et al.*, 1999). Thus, significant contributions of channel precipitation could in part explain why fractions of event NO_3^- were greatest during

Table IV. Fractions of event NO_3^- and event H_2O at peakflow for the five watersheds monitored in upper Spring Creek

Storm number/date	Watershed									
	Forested		Urban		Agricultural		Mixed LU Houserville		Mixed LU Rock Road	
	Event NO_3^-	Event H_2O	Event NO_3^-	Event H_2O	Event NO_3^-	Event H_2O	Event NO_3^-	Event H_2O	Event NO_3^-	Event H_2O
1. 23 March 2005	0.50	0.01	1.00	0.91	—	0.09	—	0.25	<0.01	0.07
2. 28–29 March 2005	0.19	0.62	0.35	0.97	—	<0.01	0.03	0.46	0.05	0.47
3. 5 July 2005	1.00	0.05	—	1.00	0.06	0.13	0.11	0.18	0.01	0.03
4. 31 August 2005	0.29	0.43	—	0.65	<0.01	0.17	0.12	0.51	0.08	0.48
5. 7 October 2005	—	0.58	0.22	0.68	<0.01	0.21	0.07	0.58	0.06	0.69
6. 16 November 2005	0.23	0.02	0.31	0.19	<0.01	0.01	0.05	0.48	—	—
Mean ^a	0.44	0.23	0.47	0.69	0.02	0.13	0.05	0.41	0.02	0.29
Standard error ^a	0.15	0.13	0.16	0.16	0.01	0.04	0.02	0.07	0.02	0.12

^a Means and standard errors were only calculated for events where both event NO_3^- and event water could be estimated.

small storms that generated small event water fractions (<0.05).

In addition to channel precipitation, it could be argued that wash-off of NO_3^- in dry deposition from soil and vegetated surfaces was important during small storms. Studies of N deposition in forested watersheds have estimated that dry deposition is a significant pathway of N input, comprising 46% (Lovett and Lindberg, 1993) to 80% (Lindberg *et al.*, 1986) of total N deposition. In the current study, one sample of dry NO_3^- deposition collected in mid-November 2005 had a $\delta^{15}\text{N}-\text{NO}_3^-$ value of $+9.9\text{‰}$ and a $\delta^{18}\text{O}-\text{NO}_3^-$ value of $+68.5\text{‰}$. The $\delta^{18}\text{O}-\text{NO}_3^-$ value measured in dry NO_3^- deposition was similar to that measured in precipitation; however, $\delta^{15}\text{N}-\text{NO}_3^-$ measured in dry NO_3^- deposition was at least 5‰ greater than $\delta^{15}\text{N}-\text{NO}_3^-$ measured in precipitation (Figure 3). Comparable differences between $\delta^{15}\text{N}-\text{NO}_3^-$ measured in dry and wet deposition were observed in a recent study conducted in the Appalachian Plateau region of Ohio, Pennsylvania and New York (Elliott *et al.*, in press). Future studies in forested watersheds may be able to take advantage of the $\delta^{15}\text{N}-\text{NO}_3^-$ difference between wet and dry deposition to estimate the relative contribution of these important atmospheric sources in event NO_3^- .

Urban, karst watershed response to storm events. NO_3^- sources: Changes in $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ from baseflow to peakflow were significant on the urban watershed (Figure 1) during all six storm events in 2005. Baseflow to peakflow changes in $\delta^{18}\text{O}-\text{NO}_3^-$ were the most substantial, with consistently upward shifts in the direction of atmospheric NO_3^- ranging in magnitude from $+7.3\text{‰}$ (7th October) to $+47.4\text{‰}$ (31st August) (Figure 5). Indeed, results from a two-tailed *t*-test indicated that $\delta^{18}\text{O}-\text{NO}_3^-$ during peakflow (mean = $+30.8\text{‰}$, SD = 14.6) was significantly higher than $\delta^{18}\text{O}-\text{NO}_3^-$ in baseflow (mean = $+3.7\text{‰}$, SD = 1.7) for all six storms ($p = 0.001$). In addition, $\delta^{15}\text{N}-\text{NO}_3^-$ decreased from baseflow to peakflow during five storm events (mean decrease = -5.2‰) with the November 16 storm being the only exception (slight increase of $+1\text{‰}$) (Figure 5).

Based on the urban NO_3^- isotope results, it was clear that atmospheric NO_3^- was the most important new source of NO_3^- at peakflow, although additional NO_3^- contributions may have also come from the flushing of detritus stored in storm sewers and on impervious surfaces. We applied the same two-component model used for the forested watershed (Equation 2) to estimate the importance of atmospheric NO_3^- contribution during storms relative to other NO_3^- source inputs. In this case, we assumed that the average terrestrial $\delta^{18}\text{O}-\text{NO}_3^-$ value was $+4\text{‰}$ (mean $\delta^{18}\text{O}-\text{NO}_3^-$ from six baseflow samples collected from the urban watershed), peakflow $\delta^{18}\text{O}-\text{NO}_3^-$ was $+30.8\text{‰}$ (mean of six storm events) and atmospheric $\delta^{18}\text{O}-\text{NO}_3^-$ was $+44.3\text{‰}$ (mean of 21 samples). The result of this calculation suggested that

the atmosphere contributed as much as 67% of NO_3^- at peakflow on this particular urban watershed.

Indeed, others have also noted the importance of atmospheric NO_3^- in urbanizing watersheds during high flows. For example, Anisfeld *et al.* (2007) studied two mixed land-use watersheds in Connecticut and Burns *et al.* (2009) monitored several suburban watersheds in central New York during high stream flow using $\delta^{18}\text{O}-\text{NO}_3^-$. Results from both studies implied that NO_3^- in atmospheric deposition could contribute upwards of 50% of the NO_3^- in these watersheds. Earlier studies by Ging *et al.* (1996) and Silva *et al.* (2002) using $\delta^{18}\text{O}-\text{NO}_3^-$ in two urbanized watersheds in Austin, Texas, also pointed to the importance of atmospheric NO_3^- in stormflow due to the influence of runoff from impervious surfaces.

Results from the current study point to an even greater contribution of NO_3^- from atmospheric deposition to urban streams than what has previously been reported. Clearly, some portion of this atmospheric NO_3^- is from wet deposition in runoff, and the remainder is from the wash-off of dry deposition that has built-up over time before the storm event. Unfortunately, with only one measurement of the $\delta^{18}\text{O}-\text{NO}_3^-$ and $\delta^{15}\text{N}-\text{NO}_3^-$ in dry deposition (Figure 3), it is not possible to estimate the relative importance of wet and dry deposition during individual events, but future work in urban watersheds should focus on characterizing NO_3^- isotopes in both wet and dry deposition to potentially separate out these two important sources of NO_3^- in urban runoff.

NO_3^- flow pathways: The predominance of atmospheric NO_3^- deposition in runoff as indicated by the changes in NO_3^- stable isotopes from baseflow to peakflow is important because it points to overland flow, including direct runoff from impervious surfaces, as a principal flow pathway for water and NO_3^- during storm events on the urban watershed. Results from hydrograph separations using $\delta^{18}\text{O}-\text{H}_2\text{O}$ are consistent with this generalization, as peakflows were dominated by the event water fraction (mean = 0.69) during most events, particularly the storms occurring on 23rd March, 28th–29th March and 5th July (Table IV). This finding agrees with past work on urbanized watersheds consistently showing overland flow to be an important flow pathway for water and solutes (Paul and Meyer, 2001).

Given the importance of event water on the urban watershed and the aforementioned changes in NO_3^- stable isotopes from baseflow to peakflow, particularly $\delta^{18}\text{O}-\text{NO}_3^-$, one might anticipate that event NO_3^- fractions would be correspondingly high. Interestingly, event NO_3^- fractions were generally less than 0.5 (Table IV), which did not seem consistent with the observed changes in NO_3^- stable isotopes during storm events. In particular, long-duration events occurring on 28th–29th March and 7th October (Table II) had event NO_3^- fractions less than 0.35, whereas event water fractions were generally greater than 0.68. Because the entire watershed is not completely impervious (Table I), there would be many opportunities for overland flow from parking lots and

roads to flow onto grassy surfaces, infiltrate and shift to shallow subsurface flow pathways. Although a transfer of overland flow to shallow subsurface flow may not have substantially altered the $\delta^{18}\text{O}\text{-H}_2\text{O}$ signal from precipitation, it may have promoted assimilation of event NO_3^- as water infiltrated into the soil. Conversion to shallow subsurface flow also may have resulted in the flushing of a mixture of stored NO_3^- sources that had lower $\delta^{18}\text{O}\text{-NO}_3^-$ values than atmospheric deposition. Either of these two mechanisms operating independently or in tandem could help to explain why event NO_3^- fractions were lower than event water fractions during these long-duration storm events.

In contrast to long-duration events, the two most intense storms on 5th July and 31st August would be expected to generate correspondingly high event water and event NO_3^- fractions due to the fact that both of these events occurred within the span of about 1 h (Table II), thereby limiting any opportunities for infiltration and NO_3^- storage or assimilation. Despite the fact that changes in $\delta^{18}\text{O}\text{-NO}_3^-$ from baseflow to peakflow were quite high during these two storms (Figure 5), indicating an important contribution from atmospheric NO_3^- , we were unable to characterize the event NO_3^- fractions in these two events due to an inability to sample time variations in very high-intensity events using the resin method of NO_3^- isotope analysis, which requires large quantities of water. During longer and less intense storms such as the one on 28th–29th March, $\delta^{18}\text{O}\text{-NO}_3^-$ was shown to be quite variable and changed by as much as 35‰ during the course of the storm (Buda and DeWalle, in press). If variations of this magnitude also occurred during the more intense storms on 5th July and 31st August, then potentially higher levels of $\delta^{18}\text{O}\text{-NO}_3^-$ may simply have been missed during both storms. If one of these missed values was associated with a precipitation burst that contributed to the measured peakflow on the urban watershed, this would certainly have affected the calculation of event NO_3^- . Indeed, the $\delta^{18}\text{O}\text{-NO}_3^-$ in precipitation from both storms was much less than the $\delta^{18}\text{O}\text{-NO}_3^-$ measured in peakflow on the urban watershed, which resulted in event NO_3^- fractions that were much greater than one, a physical impossibility. Clearly, future work using tracers to estimate event fractions of NO_3^- on urban watersheds should include provisions to more intensively sample precipitation over time. The use of the denitrifier method (Sigman *et al.*, 2001; Casciotti *et al.*, 2002), which requires substantially lower volumes of event water for isotope analysis, may help to resolve this issue.

Non-urban, karst watershed response to storm events.

NO_3^- sources—agricultural watershed: On the agricultural watershed (Figure 1), changes in $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ from baseflow to peakflow were notably smaller and more variable during storms (Table III) as compared with the forested (Figure 4) and urban (Figure 5) watershed responses. Changes in $\delta^{15}\text{N}\text{-NO}_3^-$ and $\delta^{18}\text{O}\text{-NO}_3^-$ during storms typically were less than

$\pm 1.5\text{‰}$. Stable NO_3^- isotopes measured during storms on the agricultural watershed indicated that NO_3^- sources probably did not change much with a fairly constant mixture of NO_3^- from manure/septic system effluent and/or soil-derived sources present before and during storm events.

NO_3^- sources—mixed land-use watershed at Houserville: Changes in NO_3^- stable isotopes during storm events at the mixed land-use site at Houserville (Figure 1) were similar in magnitude to those observed on the agricultural watershed. Observed changes in $\delta^{15}\text{N}\text{-NO}_3^-$ from baseflow to peakflow typically were small (less than $\pm 0.5\text{‰}$) (Table III). The one exception occurred on 23rd March, when $\delta^{15}\text{N}\text{-NO}_3^-$ decreased by 2.7‰. This decrease in $\delta^{15}\text{N}\text{-NO}_3^-$ was potentially due to runoff from melting snow, which had a $\delta^{15}\text{N}\text{-NO}_3^-$ value of -0.6‰ (Figure 3). Changes in $\delta^{18}\text{O}\text{-NO}_3^-$ were slightly more significant during storms than changes in $\delta^{15}\text{N}\text{-NO}_3^-$, and these changes typically were positive ($+1.3\text{‰}$ to $+4.2\text{‰}$). The largest increase of $+4.2\text{‰}$ occurred on 31st August, which was a high-intensity thunderstorm (48 mm h^{-1}), and therefore this change likely reflected the influence of NO_3^- from precipitation. Ultimately, the small changes in NO_3^- isotopes from baseflow to peakflow at the mixed land-use site in Houserville indicated that NO_3^- sources did not change much during storm events. The source mixture appeared to consist of mostly soil N and manure sources, although a more complex mixture of NO_3^- sources from upstream forested, agricultural and urban land-use inputs cannot be ruled out because longer transport times and biogeochemical transformation processes may have effectively altered the initial NO_3^- isotope source signals (Mayer *et al.*, 2002; Burns *et al.*, 2009).

NO_3^- sources—mixed land-use watershed at Rock Road: The mixed land-use site at Rock Road (Figure 1) generally behaved differently than the upstream site at Houserville during storms, presumably due to the influence of sewage effluent at baseflow (Figure 3). Although changes in $\delta^{18}\text{O}\text{-NO}_3^-$ were generally minor during storms ($+0.1\text{‰}$ to $+2.7\text{‰}$) (Figure 6), much more substantial changes in $\delta^{15}\text{N}\text{-NO}_3^-$ were observed during storm events with the predominant movement being towards a lower $\delta^{15}\text{N}\text{-NO}_3^-$ value in the range of soil N. Essentially, the high $\delta^{15}\text{N}\text{-NO}_3^-$ at baseflow (Figure 3) caused by the UAJA sewage effluent appeared to be diluted during storms due to the addition of a lower $\delta^{15}\text{N}\text{-NO}_3^-$ signal from upstream sources and possibly soil N. Sewage effluent contributions to stream flow appear to be easily traced by using $\delta^{15}\text{N}\text{-NO}_3^-$ isotopes.

NO_3^- flow pathways on the non-urban, karst watersheds: Two-component separation models were used to provide information regarding potential water and NO_3^- flow path dynamics on the three non-urban karst watersheds. Mean event water fractions (Table IV) on the mixed land-use watersheds at Houserville (mean = 0.41)

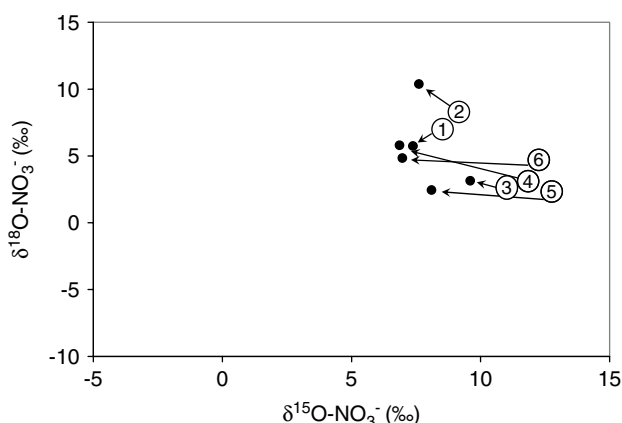


Figure 6. Mixed land-use watershed at Rock Road $\delta^{18}\text{O}-\text{NO}_3^-$ versus $\delta^{15}\text{N}-\text{NO}_3^-$ for all six storm events sampled during 2005 showing baseflow (open numbered circle) to peakflow (closed black circle) changes in NO_3^- stable isotopes. Numbers are used to label each storm event (1 = 23rd March; 2 = 28th–29th March; 3 = 5th July; 4 = 31st August; 5 = 7th October; 6 = 16th November)

and Rock Road (mean = 0.29) as well as the agricultural watershed (mean = 0.13) suggested that pre-event water was typically the predominant water source during most storm events. An exception to this occurred during the most intense storm on 31st August (Table II), where much larger event water fractions were observed on the agricultural (0.17) and mixed land-use watersheds at Houserville (0.51) and Rock Road (0.48). In addition to mostly low event water fractions, mean fractions of event NO_3^- also were low on the mixed land-use watersheds at Houserville (mean = 0.05) and Rock Road (mean = 0.02) as well as the agricultural watershed (mean = 0.02). These results suggested that the water and NO_3^- delivered during storms on the three non-urban karst watersheds followed mostly subsurface ground water flow pathways.

Additionally, fractions of event NO_3^- were generally much less than fractions of event water on all three non-urban karst watersheds, which suggested that flushing of stored NO_3^- and assimilative processes may have been important. With regard to flushing potential, the carbonate aquifers that underlie the valleys in the non-urban karst watersheds promote substantial storage of ground water (Fulton *et al.*, 2005) in pipes and solution cavities (White, 1988). This ground water can be released slowly during storm events (White and Reich, 1970) and can flush of a mixture of stored NO_3^- sources that likely have been subject to biogeochemical processing and transformation. Furthermore, deep soils in the karst valleys also may have promoted storage and assimilation of event NO_3^- through the infiltration of incoming precipitation and nearby sources of surface runoff from impervious surfaces such as roads and parking lots. This process may have been especially important in the two mixed land-use watersheds at Houserville and Rock Road, where impervious cover was more prominent than in the agricultural watershed (Table I), and event NO_3^- fractions were substantially lower than event water fractions for most storm events.

CONCLUSIONS

Nitrate-stable isotopes were useful for showing how NO_3^- sources changed from baseflow to peakflow during storm events in the Spring Creek watershed. On the forested, sandstone watershed, NO_3^- predominately was a mixture of event atmospheric and older stored soil sources at peakflow, and the relative importance of these sources appeared to depend on storm size. During small storms (<35 mm rainfall), fractions of event NO_3^- were greater than fractions of event water at peakflow, which suggested that channel precipitation and/or wash-off of dry-deposited NO_3^- from vegetated surfaces represented potentially important NO_3^- sources. During large storms (>35 mm rainfall), fractions of event NO_3^- less than fractions of event water at peakflow suggested that shallow subsurface flow pathways caused by steep terrain and shallow soils with high infiltration capacity over relatively impermeable sandstone and shale bedrock were more important NO_3^- delivery mechanisms to stream water.

On the urban watershed, large changes in $\delta^{15}\text{N}-\text{NO}_3^-$ and $\delta^{18}\text{O}-\text{NO}_3^-$ during storm events clearly showed that atmospheric NO_3^- sources (wet + dry deposition) were predominant during peakflow conditions, and that no other significant urban NO_3^- sources beyond those from the atmosphere were detectable. This was especially true for short-duration, high-intensity type events. In contrast, two long-duration events had event NO_3^- fractions that were less than event water fractions, suggesting that storage and assimilation and/or flushing of stored NO_3^- can be important on the urban watershed, despite contributions of atmospheric NO_3^- in wet and dry deposition.

On the agricultural and mixed land-use karst watersheds, a much different response to storms was observed. Small changes in NO_3^- isotope values from baseflow to peakflow on the agricultural watershed and at the mixed land-use site in Houserville suggested that NO_3^- sources did not change much during storms on these two karst watersheds. Further downstream at the Rock Road mixed land-use site, enriched values of $\delta^{15}\text{N}-\text{NO}_3^-$ served as an excellent tracer for upstream sewage effluent discharges during baseflow conditions, but these values were quickly diluted during storm events due to fluxes of NO_3^- from upstream sources with lower $\delta^{15}\text{N}-\text{NO}_3^-$ signals. In addition to small changes in isotopes during storm events, fractions of event NO_3^- were much less than fractions of event water. This indicated that event effects were potentially muted by the assimilation of event NO_3^- in deeper soils and/or the delivery of stored NO_3^- via subsurface ground water flow pathways. The results of this study illustrate how NO_3^- isotopes and $\delta^{18}\text{O}-\text{H}_2\text{O}$ can be combined to show major differences in water and NO_3^- delivery mechanisms during storms between forested uplands and karst valleys, and confirm the dominance of overland flow pathways in fully urbanized watersheds during high-intensity storm events.

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